Glass and Ceramics Vol. 59, Nos. 11 – 12, 2002

SCIENCE FOR GLASS PRODUCTION

UDC 666.1.022.8

PHASE TRANSFORMATIONS IN MOISTENED GLASS BATCHES UNDER COMPACTION

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Translated from Steklo i Keramika, No. 12, pp. 38 – 42, December, 2002.

The phase transformations in glass batches at all stages, including moistening, compaction, and drying, are investigated, and criteria for moldability of glass batches are proposed. A correlation between the main process parameters of granulation (moisture, granule formation duration, and mechanical strength of granules) and the proposed criteria is established and the possibility of using them in selection of the batch compaction method and conditions is demonstrated.

One of the ways for increasing the efficiency of glass production involves using compacted glass batches, which makes it possible to substantially improve the main production parameters, to solve environmental problems, and to develop energy-saving technologies. Despite all this, compaction so far has not been widely implemented in the domestic glass-production practice. The main reason is the absence of effective technologies that would ensure stable performance at the particular production facility and absence of universal methods for evaluating the molding properties of glass batches, which could be used in selecting compaction methods and conditions.

Researchers from the State Institute of Glass, D. I. Mendelev Russian Chemical Engineering University, and Moscow Institute of Chemical Machinery have made significant contributions in researching properties of glass batches and developing efficient methods for their compaction. The granulation methods developed by them, including palletizing, extrusion, and compression on a roller press for various types of glasses, have successfully passed industrial testing and have been implemented at several factories [1, 2].

Extensive research in studying the capacity of disperse materials for wet granulation by pelletizing was carried out by a group of scientists at the Tomsk Polytechnic University directed by V. M. Vityugin. The authors believe that the kinetics of granule formation depends on the aqueous-physical and structural-mechanical properties of moist disperse materials, i.e., their clotting ability. A set of criteria was developed for a wide range of disperse materials that reflected the ability of materials for wet aggregation and on the basis of their experimental verification, a classification of disperse materials based on the difficulty of nodulizing them was proposed [3, 4]. However, the criteria for evaluation of pelletizing capacity proposed by these authors are mainly applicable to insoluble disperse materials.

The specific feature of glass batches is the presence of a great number of components that are chemically active with respect to water and to each other. The use of palletizing criteria not taking into account all complexity of the physicochemical phenomena taking place in moistening and compacting of batches limits the possibility of technological control of the number of granules and efficiency of machinery.

The present study considers phase transformations in glass batches at all stages of their preparation, including moistening, compaction, and drying of batches and proposes criteria of moldability of glass batches.

We have investigated industrially used batches for various types of glasses (Table 1). Such batches differ in their component composition and primarily in the content of water-soluble components (20.41 – 66.50%) and components capable of binding water in crystal hydrates (11.35 – 25.94%).

Glass batches by their granulometric composition belong to coarsely disperse materials. The majority of the considered batches to an extent of over 70% consist of particles sized more than 0.16 mm. An exception is represented by batches for optical glasses, in which the content of the fraction less than 0.16 mm is equal to 57.80 – 72.00%.

Several methods of compacting glass batches are known: granulation by pelletizing, extrusion, vibration granulation,

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0361-7610/02/1112-0424$27.00

pressing, etc. Some scientists believe that granulation by palletizing is the simplest and the most cost-effective method.

In the context of physicochemical mechanics, the kinetics of granule formation represents a complex process of interactions between the solid (S), liquid (L), and gaseous (G) phases. The main factors determining the effectiveness of this process are the properties of the phases and the nature of their reactions.

The results of studying phase transformations occurring in moistening of glass batches and individual water-active components using microscopic and x-ray phase analysis methods revealed the following:

– dissolution lowers the ratio of the solid to the liquid phase (S/L) and increases the gas phase content; it is mainly the finely disperse component of the solid phase that passes into solution;

– crystallization increases the ratio S/L due to the formation of a great number of small crystals with a high specific surface area and their subsequent growth.

The main crystallizing material capable of forming thermally unstable crystal hydrates of different degrees of hydration is sodium carbonate. Moistening of soda with water (18 – 20°C) is accompanied by complete dissolution of small (less than 0.1 mm) particles and the formation of a dense crystal-hydrate shell on the surface of incompletely dissolved grains, which consists of needle-shaped crystals $Na_2CO_3 \cdot H_2O$ and prismatic crystals $Na_2CO_3 \cdot 2.5H_2O$ (Fig. 1*a*). Decahydrate crystal hydrates $Na_2CO_3 \cdot 10H_2O$ of tabular shape are predominantly formed in the liquid phase volume (Fig. 1*b*). When soda is moistened with hot water (40 – 60°C), crystal decahydrates do not emerge even under a high degree of supersaturation of the solution. Moistening of soda with potash solution is accompanied by the formation of predominantly needle-shaped crystals $Na_2CO_3 \cdot H_2O$ (Fig. 1*c*).

Thus, the processes of dissolution and crystallization in moistened glass batches result in a modification of the phase ratio (S – L – G), of their quantitative and qualitative composition, and, accordingly, of the molding properties of batches.


a


b


c

Fig. 1. Microphotos of soda moistened by water (*a*, *b*) and by potash solution (*c*).

The existence of phase transformations is corroborated by the x-ray phase analysis data (Fig. 2).

The preformed studies made it possible to expand the existing concept of the mechanism of granule formation in glass batches. The process of nucleation and formation of granules can be represented as follows. The dissolution processes decrease the ratio S/L and increase the mean effective

TABLE 1

Batch for glass production	Mass content of components in batch, %			Duration, min			Method for batch compaction
	water-soluble	binding water in crystal hydrates	soda	active moisture consumption at 18 – 20°C	active moisture consumption at 50 – 60°C	solidification	
Optical	35.82	11.35	11.35	9.66	10.00	> 120	Granulation by palletizing
Household	24.43	24.43	19.43	7.20	10.00	40	Thermogranulation with a binder
Electrovaccum	66.50	15.80	15.80	8.75	10.00	120	Pressing, extrusion
Electroengineering	25.94	25.94	20.06	6.50	8.20	30	Pressing
Cut crystal	28.59	20.08	2.08	6.40	7.00	> 120	Extrusion
Container	20.69	20.69	17.99	8.00	10.00	50	Thermogranulation, pressing
Sheet	20.41	20.41	17.44	8.20	10.00	53	Pressing
Milky	21.63	21.63	21.63	3.30	10.00	15	The same

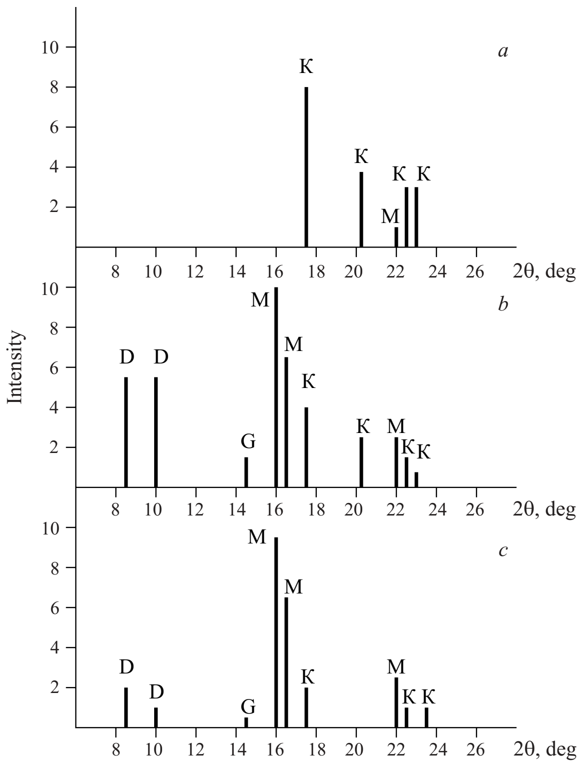

Fig. 2. X-ray diffraction diagram of soda in air-dry state (*a*), moistened with water (*b*) and potash solution (*c*): K) Na_2CO_3; M) $Na_2CO_3 \cdot H_2O$; G) $Na_2CO_3 \cdot 2.5H_2O$; D) $Na_2CO_3 \cdot 10H_2O$.

distance between particles, lowering the capillary adhesion strength. Furthermore, the decrease in the strength of coagulation contacts is facilitated by gas bubbles forming in the dissolution of the salts. The time of existence of the coagulation structure for soda-containing batches is not long and constitutes 10 – 15 sec. As the liquid phase becomes saturated with dissolved compounds and reaches a certain degree of supersaturation, crystallization centers (seeds) are formed.

The emergence of a great number of small crystals (less than 0.1 mm) with a high specific surface area increases the ratio S/L and the strength of adhesion of particles in the batch layer. The batch acquires sufficient plasticity for the formation of strong granule nuclei. As the granules condense as a consequence of multiple impacts against the edge of the granulator tray, the particles get nearer to each other, the thickness of water interlayers decreases, and the strength of adhesion increases. Excess moisture is squeezed onto the granule surface, which provides for adhesion of dry particles and the growth of granules.

The evolution of crystallization processes in thin liquid interlayer leads to a further increase in the ratio of S/L and increases the strength of granules due to the transformation of a part of the coagulation contacts into stronger crystallization contacts. The stage of granule growth is mainly determined by the intensity of the mass-transfer processes in the liquid phase, which exists in the capillary-mobile state. The evolution of the crystallization and recrystallization processes contributes to the stabilization of the granule structure at the stage of rolling. The transformation of a coagulation-crystallization structure into a crystallization structure is accomplished by removal of the liquid phase in drying or its transition to the fixed state.

Taking into account the results of the integrated studies of aqueous-physical and structural-mechanical properties of glass batches, it is possible to propose active moisture consumption and solidification of moistened batches as criteria of their molding properties [5]. It is established that the specified parameters decrease as the content of crystallizing compounds in the batch (primarily soda ash) increases and increase with increasing temperature (Table 1).

The mathematical description of the kinetic curves for the considered batches is as follows:

$$\frac{V}{S} = K_{sp}(1 - e^{-T/t}),$$

where V/S is the specific volume of absorbed moisture (V is the volume of absorbed moisture; S is the area of the sample surface); K_{sp} is the proportionality coefficient; T is the time constant; t is the time of impregnation.

The proportionality coefficient characterizes the total volume of absorbed moisture and for the considered batches at a temperature of 20°C is equal to 0.21 – 0.66 ml/cm^2, and at 50°C it is equal to 0.28 – 0.73 ml/cm^2.

As a consequence of multiple experiments in granulation of glass batches on a tray granulator, the correlation between the main parameters of the process (moisture, granule formation duration, and mechanical strength of granules) and the time of active moisture absorption and batch solidification was established. These criteria can be used to select the method of compaction of glass batches and its conditions (Table 1). The selection of the moistening method and the layout of the work zones on the granulator tray taking into account the mechanism of granule formation substantially stabilized granule formation and improved the quality of granules.

The main disadvantages of compaction by pelletizing is the high moisture content and the low mechanical strength of granules. There are different ways to improve the technological properties of granules: use of binding additives, thermal granulation, drying. The use of such binders as sodium silicate solution, potash, or carbamide leads to a slight (2 – 5%) decrease in the moisture of granules, whereas their strength remains low (less than 300 – 400 g per granule).

An effective method for compacting glass batches with a high content of components capable of binding water in crystal hydrates is thermal granulation. As glass batches are heated to 40 – 60°C, highly hydrated crystal hydrates of sodium and potassium carbonate and sodium sulfate decompose and release water that acts as a batch plastifier. Thermal granulation made it possible to decrease the moisture content of raw granules 3 – 4 times, and cold air blowing (below

10°C) at the granulator outlet increased the strength 3 – 5 times [6].

The most effective and common method for improving the technological properties of granules is their drying. Studies carried out at the Silicate Technology Department of the Tomsk Polytechnic University made it possible to identify the effect of heat treatment conditions on the structure, mechanical strength, and chemical homogeneity of granules. A dried granule has a zonal structure: a dense surface layer and a relatively loose central part. This causes their chemical inhomogeneity (Fig. 3).

According to the chemical analysis data, the content of insoluble residue decreases from the center of the granule to its periphery, and the content of the alkali components changes in the opposite direction. The reason for the zonal structure of the granules is the mass transfer of capillary-mobile liquid, which in glass batches represents a solution of components that are chemically active with respect to water and to each other. The degree of inhomogeneity of granules depends on the heat-treatment conditions.

The performed studies made it possible to establish the optimum drying condition for granules. It is recommended to implement drying of batches containing chemically active components (below 15%) in two stages. At the first stage, the temperature should not exceed 100°C, at the second stage it can be raised to 300 – 400°C. It is advisable to blow batches with a high (over 15%) content of crystallizing components with cold air for the purpose of increasing the thermal resistance of granules before the high-temperature (300 – 400°C) drying [7]. However, one should bear in mind that the introduction of the drying operation into the technology of granulated batch production involves higher capital and energy expenditures.

The method of compacting glass batches on a roller press has been widely used lately. This simple and efficient method of compaction makes it possible to eliminate the stage of drying from the technological scheme. An analysis of the glass batch compacting plant, including the roller press operating at the Tomsk Electric Bulb Factory, demonstrated several significant disadvantages: a high content of the fraction below 1 mm (30 – 40%) in the compacted batches; losses of batch in the form of crumbling waste up to 10%, unstable chemical composition of molded samples.

As a consequence of studies performed at the Silicate Technology Departments it was found that one of the reasons for the unsatisfactory quality of compressed products is incomplete formation of their crystallization structure before they are loaded into a glass-melting furnace, which is mainly due to their increased temperature (40 – 50°C). Forced cooling of pressed articles using cold air (less than 10°C) at the exit from the deformation zone, as well as using potash solution for batch moistening, have a positive effect on the strength of articles and, consequently, on the yield of the standard fraction. At the same time, it is necessary to thoroughly select the molding pressure and the rotational speed of the roll. A high pressure in the compression zone

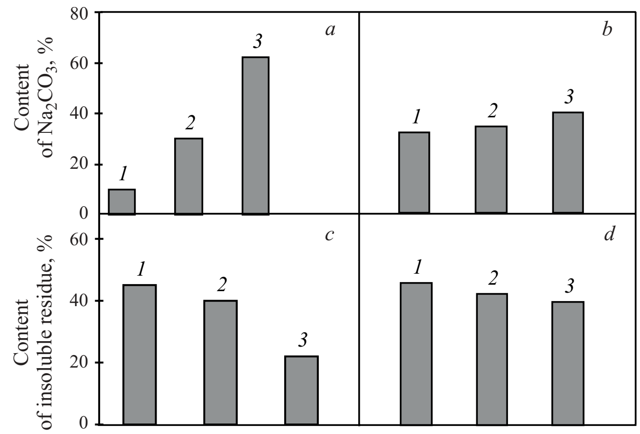

Fig. 3. Histograms of distribution of Na_2CO_3 and insoluble residue in the granules volume drying at 120°C (*a*, *c*) and 20°C (*b*, *d*): *1*) center of the granule; *2* and *3*) periphery layers.

(200 – 300 MPa) leads to the emergence of defects in the compressed article structure, which impedes uniform distribution of the liquid phase and the formation of a coagulation structure ensuring the initial strength of the article. The pressure in the compression zone should not exceed 10 – 15 MPa. A decrease in the rotational speed of the rolls enables one to decrease the pseudoliquefying effect in the deformation zones and the conveyor belt velocity, which reduces the amount of waste at all stages of the process.

The results of the integrated studies and their correlation with the possibilities and conditions of individual production facilities made it possible to develop a technology for granulating glass batches for optical, cut crystal, and household glasses using the pelletizing method, to issue practical recommendations for improving the compaction technology on a roller press, and to develop the thermal granulation technology for sheet-glass batch and for lead-bearing batches for optical glasses (USSR Inventor’s Certif. Nos. 1296519 and 700469).

Industrial testings carried out at the Lytkarinskii, Nikol’skii, Andzhero-Sudzhenskii, and Tomskii glass works indicated that the use of compacted batches makes it possible to decrease by 6 – 7 times the entrainment of their finely dispersed components in the zone of furnace loading, to increase by 25 – 30% the melting rate, to increase the yield of standard granules (pressed articles) on a roll press by 90% due to a set of activities intended for their strengthening at the exit from the working zone, and to improve labor conditions.

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